

Contribution of the Jahn-Teller effect in the electronic Raman scattering in $\text{MgO}:\text{Co}^{2+}$

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A theoretical study of the electronic Raman scattering of MgO with substitutional Co^{2+} impurities is presented in this paper, and the Jahn-Teller interaction is employed to calculate the line shape. The contribution to the Raman scattering discussed here is different from the phononic contribution studied by other authors. In their calculation, they have implicitly assumed the validity of the Born-Oppenheimer approximation, an assumption that is not valid for the lowest levels of Co^{2+} in MgO . The electronic Raman intensity is given by an approximate formula that contains the time correlation function of transition operators between the few electronic states of Co^{2+} that are close to the ground state. To obtain these correlation functions we employ Green's functions, decoupling the equation of motion at a convenient stage of the calculation. Only the normal modes of the complex formed by Co^{2+} and the six nearest O^{2-} ions have been included in the Jahn-Teller interaction, and they have been expressed as a series of all the lattice phonons. The theoretical phonon spectrum of MgO has also been replaced by a simpler analytical expression that gives its more important features. Most of the parameters that appear in the calculation have been derived from other properties of the system. There is a fairly good agreement between the measured Raman spectrum and the one calculated here. In particular, the relative position of the two $\Gamma_6 \rightarrow \Gamma_8$ and $\Gamma_6 \rightarrow \Gamma_8$ transitions is well explained by the model. The theory also predicts a splitting of the $\Gamma_6 \rightarrow \Gamma_8$ line into a doublet, a fact that is experimentally observed.

I. INTRODUCTION

In this paper we present a theoretical study of the electronic Raman scattering of MgO with substitutional Co^{2+} impurities, and we show that the dynamical Jahn-Teller (JT) interaction plays an important role in the corresponding line shape.

Pure crystalline MgO has the rocksalt structure, and the Raman scattering by a single phonon is forbidden because there is lattice translational invariance and all the ions are a center of inversion. This rule is broken by the presence of impurities, and a modified Raman spectrum is observed in their presence. Several experimental and theoretical studies of this impurity-induced Raman spectrum have been reported so far. A classical example is that of the Tl^+ -doped alkali halides studied by Harley *et al.*,¹ who provided several references concerning this type of experiment. The case of MgO with Co^{2+} as impurity was reported by Mon² and Billat *et al.*,³ and a more detailed study with both Fe^{2+} and Co^{2+} as impurities was reported by Billat *et al.*⁴ More recently, Guha⁵ reported measurements at 18 K of $\text{MgO}:\text{Co}^{2+}$.

One of the basic assumptions in the theory reviewed by Harley¹ is that the Born-Oppenheimer approximation⁶ (BOA) is valid, implying that the electronic ground state of the system should be well separated in energy from all the electronic excited states. The system is then assumed to remain in that ground electronic state after the Raman scattering, while a single phonon is created or destroyed in the process. Mon,² Billat *et al.*,³ and Guha⁵ supposed

that this was the case in the spectra they studied, making an exception with the 934-cm^{-1} line observed in $\text{MgO}:\text{Co}^{2+}$, that was assumed to be electronic because there are no phonons with this high frequency in the spectrum.

The spectra observed by Billat *et al.*⁴ are rather different for the two impurities Co^{2+} and Fe^{2+} , their intensity maxima not being far apart from the lowest electronic excitations of those two ions. These considerations lead us to investigate the electronic Raman scattering of the impurity as an alternative mechanism, i.e., a process in which the electronic state of the impurity in the final state is different from the initial one, while the vibrational state of the MgO lattice remains the same. The electronic Raman scattering has been already measured in several trigonal compounds^{7,8} of Fe^{2+} and Co^{2+} , in cubic KZnF_3 doped⁹ with Co^{2+} and in several other systems summarized in a recent review article by Lockwood.¹⁰

We believe that in our system, the two mechanisms contribute to the spectrum, but we will only consider here the electronic Raman scattering of Co^{2+} so that the characteristics of this effect are more clearly emphasized. We will discuss at the end of this paper the superposition of the two contributions. As the electronic Raman scattering of a single Co^{2+} is not sufficient to describe the observed spectrum, particularly in the 300-cm^{-1} region where a single line would be expected and a doublet is observed, we will consider the interaction between the Co^{2+} and the phonons. However this interaction takes a rather special form in the present problem, where the Born-

Oppenheimer approximation is not valid. The Co^{2+} enters substitutionally in the lattice and retains the cubic symmetry¹¹ of MgO. The Jahn-Teller (JT) theorem^{12,13} then allows a coupling between the electronic states of Co^{2+} and the displacements of the neighboring ions. This coupling is linear in those displacements and is the JT interaction, which has been employed to study the spin-lattice relaxation¹⁴ of Co^{2+} in MgO, and will provide a linewidth to the mechanism proposed here. Although the overall symmetry of the Co^{2+} ion is cubic, the instantaneous configurations of lower symmetry produced by the displacements of the neighboring ions affect the properties of the system through the JT interaction, and this is then named the dynamical JT effect.¹⁵

It is instructive to consider how the stationary states of the system are modified by the dynamical JT effect: Rather than being the product of an electronic state times a vibrational one, as they are in the Born-Oppenheimer approximation (BOA), many of these products are strongly mixed in the stationary states which are then called vibronic states. This effect is important in $\text{MgO}:\text{Co}^{2+}$ because the separation between the lowest energy states (300 cm^{-1}) falls well within the phonon spectrum, and the mixture is strong even if the interaction is weak. This strong mixture of product states is what gives an extended line shape to the electronic Raman scattering of Co^{2+} in MgO.

The dynamic JT effect has been already considered for Fe^{2+} compounds,⁷ and the diagonalization of an effective Hamiltonian with adequate reduction factors^{16,17} was employed to obtain the energies of the electronic transitions. In this case, no description of the line shape was obtained by the method.

To conclude this introduction we summarize the contents of this paper. In Sec. II we discuss the calculation of the Raman scattering in $\text{MgO}:\text{Co}^{2+}$, employing the mechanism proposed above. In Sec. IIA we discuss the model employed to describe the system paying particular attention to the JT interaction. In Sec. IIB the Raman intensity is expressed by an approximate formula that employs adequate correlation functions, and the Green's-function (GF) formalism is used in Sec. IIC to obtain these correlation functions. In Sec. IID we employ an analytical expression that has the gross features of the density of phonons to obtain the line shape predicted by our theory. In Sec. III we compare our GF calculation with the experimental spectra, and in Sec. IV we state our conclusions.

II. CALCULATION OF THE RAMAN SCATTERING FROM $\text{MgO}:\text{Co}^{2+}$

A. The vibronic Hamiltonian

The ground state of the free Co^{2+} ion is $4F(3d^7)$, and in the presence of the cubic crystal field it is split leaving $4T_{1g}$ as the lowest group of states. The $4T_{1g}$ is still degenerate in the orbital part, and one would expect a deformation that according to the JT theorem^{12,13} would leave a nondegenerate orbital part. This deformation does not occur¹¹ because the spin-orbit interaction stabilizes the cu-

bic structure¹⁸ by splitting $4T_{1g}$ into Γ_6 and Γ_7 doublets plus two Γ_8 quadruplets (see Fig. 1). The lowest level is Γ_6 and it cannot be further split by the crystal field because Co^{2+} is a Kramer's ion.¹³ We will call these 12 states "lower states," and call the remaining Co^{2+} states, that are rather far in energy from the lowest states, "higher states."

In our vibronic Hamiltonian^{14,19} we use the standard expression for the Co^{2+} ions and for the phonons. For a single Co^{2+} ion we employ the approximate JT interaction²⁰

$$H_{JT} = V_A \tau^a Q_a + V_E (\tau^\theta Q_\theta + \tau^\epsilon Q_\epsilon) + V_T (\tau^\xi Q_\xi + \tau^\eta Q_\eta + \tau^\zeta Q_\zeta), \quad (1)$$

where V_A , V_E , and V_T are the JT coefficients, the Q_γ are the normal modes of the seven-ion complex composed by the Co^{2+} and the six nearest O^{2-} and the τ^γ are the well-known²⁰ electronic operators defined in the subspace of the lower states of Co^{2+} . The three terms in Eq. (1) are associated with the irreducible representations T_{1g} , E_2 , and T_{2g} of the point group O_h .

For a single Co^{2+} one can expand H_{JT} by employing the standard basis operators^{21,22} X_{ab} that transform the state b of Co^{2+} into the state a of the same ion and the creation (a_{qs}^\dagger) and destruction (a_{qs}) operators of a phonon with wave vector q and polarization s . As we neglect the interference between different Co^{2+} ions, our result is given by the scattering of a single Co^{2+} times their number and we will not use the creation operators of ions^{23,24} that we employed in other derivations.^{19,25}

B. An approximate formula for Raman scattering

To calculate the Raman scattering, we consider the dipolar interaction between the radiation field and our system, and neglect the diamagnetic term. The interaction is

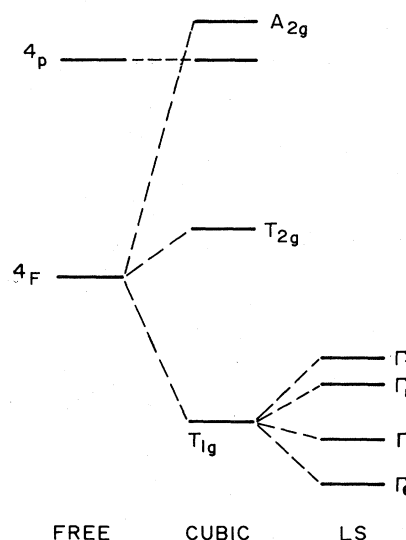


FIG. 1. Energy levels of Co^{2+} split by a cubic field and by the spin-orbit interaction. The levels are labeled by their symmetry properties.

then linear in the creation or destruction operators of photons, and at least a second-order time-dependent perturbation (TDP) is necessary.

To describe a single-phonon Raman scattering, it is customary²⁶ to treat the electron-phonon interaction H_{EP} together with the system-radiation interaction H_{SR} as a perturbation, and a third-order TDP calculation is then necessary. This treatment is appropriate when the BOA is valid, and the electronic Raman scattering is then clearly different from the phononic one. When JT ions are present, the BOA is not valid, and the H_{JT} is an electron-phonon interaction, making the distinction between the two types of Raman scattering rather difficult.

It is then convenient to separate the calculation in two contributions, which coincide respectively with the electronic and phononic contributions in the absence of JT effect. If we neglect the total electron-phonon interaction H_{EP} , we can employ the eigenstates of the total Hamiltonian to define the subspace \mathcal{E}_a , generated by those eigenstates that have the electronic part with energies close to the lowest one. We can then define H_{EP}^0 and H_{EP}' in $H_{EP} = H_{EP}^0 + H_{EP}'$ so that the only nonzero matrix elements of H_{EP}^0 are between pairs of states of \mathcal{E}_a and H_{EP}' is identically zero inside \mathcal{E}_a . To define the first contribution ("electronic"), we include H_{EP}^0 in the unperturbed Hamiltonian and treat H_{SR} in second-order TDP, so that when $H_{EP}^0 = 0$ we obtain the usual electronic Raman scattering. In this work we will approximate H_{EP}^0 by the H_{JT} given in Eq. (1).

To calculate the second contribution ("phononic") we neglect H_{EP}^0 , treat $H_{SR} + H_{EP}'$ by TDP in third order, and consider only the same initial and final electronic state inside \mathcal{E}_a . This is equivalent to the usual treatment of the one-phonon process when the impurity is not JT but has a single lower state. In the approach we are discussing, the breaking of the selection rule due to the translational invariance and inversion symmetry is effected through the change of H_{EP}' caused by the impurity presence.

The previous calculations²⁻⁵ for $\text{Co}^{2+}:\text{Mg}$ correspond to the phononic contribution discussed above, which is clearly different from the electronic contribution considered in the present paper. Employing the same technique used for a different problem,²⁵ we have derived an approximate expression for the electronic contribution to the Raman scattering intensity. It is proportional to

$$I(\omega) = \sum_{a,b} \sum_{c,d} (\epsilon' \cdot \mathbf{R}_{ab} \cdot \epsilon) (\epsilon \cdot \mathbf{R}_{cd} \cdot \epsilon') \times \int_{-\infty}^{\infty} \langle X_{ab}(t) X_{dc} \rangle \exp(-i\omega t) dt, \quad (2)$$

$$D_{aa'}(\omega) = (1/2\hbar N m_0) \sum_{\gamma, q, s} \frac{|V_{\gamma}|^2}{\omega_{qs}} |T_{qs}^{\gamma}|^2 \left[\sum_c \left[\frac{|\tau_{a'c}^{\gamma}|^2}{\omega - \omega_{ca} - \omega_{qs}} + \frac{|\tau_{ca}^{\gamma}|^2}{\omega - \omega_{a'c} + \omega_{qs}} \right] - \tau_{a'a}^{\gamma} \tau_{aa}^{\gamma} \left[\frac{1}{\omega - \omega_{a'a} - \omega_{qs}} + \frac{1}{\omega - \omega_{a'a} + \omega_{qs}} \right] \right], \quad (5)$$

where N is the number of crystal sites and m_0 is the mass of the O^{2-} ion. The sum over γ is over the six components $a, \theta, \epsilon, \xi, \eta, \zeta$ of the irreducible representations A_g, E_g, T_{2g} , and $V_a = V_A, V_{\theta} = V_{\epsilon} = V_E$, and $V_{\xi} = V_n$

where ω is the frequency of the scattered photon minus that of the incident one, which respectively have polarizations ϵ' and ϵ . The Raman tensor \mathbf{R}_{ab} is associated with the a and b states of Co^{2+} , and it is the sum over excited states of frequency dependent terms. All the influence of the intermediate states appears in these tensors, and to calculate the remaining quantities it is sufficient to operate inside the subspace \mathcal{E}_a . The operator $X_{ab}(t)$ is X_{ab} in the Heisenberg representation of the system without radiation, and $\langle A \rangle$ is the statistical average of the operator A .

The derivation of Eq. (2) employs the completeness of states to segregate the influence of intermediate states into the Raman tensors. It is valid because we have neglected H_{EP}' , making the intermediate states simple tensor products of electronic times phononic states. For resonant Raman scattering this approximation is not sufficient, and the calculation should be reformulated, but the problem might be still tractable very close to the resonance at the cost of a more elaborate theory.²⁷

C. Calculation of the line shape using Green's functions

To calculate the correlation functions $\langle X_{ab}(t) X_{dc} \rangle$ that appear in Eq. (2) we have used the double-time Green's function,²⁸ following closely the method we employed^{24,25} in similar calculations.

Two new types of GF appear in the equation of motion of $\langle\langle X_{ab}, X_{dc} \rangle\rangle_{\omega}$, and they are of the type $\langle\langle A X_{ab}; X_{dc} \rangle\rangle_{\omega}$ where $A = a_{qs}^{\dagger}$ or a_{qs} . In their corresponding equations of motion three new types of GF appear, with $A = a_{qs}^{\dagger} a_{q's'}^{\dagger}$, $A = a_{qs}^{\dagger} a_{q's'}$, or $A = a_{qs} a_{q's'}$. At this stage we decouple these GF to close the system: We neglect those with two creation or two destruction operators of phonons, and for the remaining ones we write

$$\langle\langle a_{qs}^{\dagger} a_{q's'} X_{c'c}; X_{b'b} \rangle\rangle_{\omega} = \delta_{qq'} \delta_{ss'} n_{qs} \langle\langle X_{c'c}; X_{b'b} \rangle\rangle_{\omega}, \quad (3)$$

where $n_{qs} = \langle a_{qs}^{\dagger} a_{qs} \rangle$. After solving the closed system we find

$$\langle\langle X_{aa'}; X_{b'b} \rangle\rangle = \frac{\delta_{ab} \delta_{a'b'} (P_a + P_{a'})}{[\omega - \omega_{aa'} - D_{aa'}(\omega)]}, \quad (4)$$

where $P_a = \langle X_{aa} \rangle$ is the occupation probability of the a state of Co^{2+} with energy E_a and $\omega_{aa'} = (E_a - E_{a'})/\hbar$.

The frequency-dependent self-energy is

$= V_{\xi} = V_T$. The T_{qs}^{γ} are the coefficients that connect^{14,20} the normal modes Q_{γ} to the phonons q, s , and τ_{ab}^{γ} are the matrix elements of the electronic operators τ^{γ} between the a and b states of Co^{2+} . The contribution of the sym-

metric mode A_1 cancels exactly in Eq. (5) when only states of the ${}^4T_{1g}$ subspace of Co^{2+} are included in \mathcal{E}_a . It would be necessary to include excited states ${}^4T_{1g}$ of a different configuration into \mathcal{E}_a to have a nonzero contribution of A_1 , and we neglect this contribution because of the large energy separation between the different configurations.

The correlation functions are now easily obtained from the GF in Eq. (4), and the partial contribution of the pair of Co^{2+} unperturbed states a and b to the scattered intensity in Eq. (2) is

$$I_{ab}(\omega) = (P_a + P_b) f(-\hbar\omega/k_B T) |\epsilon_s \cdot \mathbf{R}_{ab} \cdot \epsilon_0|^2 D_{ab}''(\omega) \{ [\omega - \omega_{ba} - D_{ab}'(\omega)]^2 + [D_{ab}''(\omega)]^2 \}^{-1}, \quad (6)$$

where $D_{ab}'(\omega)$ and $D_{ab}''(\omega)$ are the real and imaginary parts of $D_{ab}(\omega)$ and $f(x)$ is the Fermi function. If $D_{ab}(\omega)$ were independent of ω , Eq. (6) would represent a Lorentzian, but with the parameters employed in the present problem, the ω dependence of $D_{ab}(\omega)$ produces a rather large deformation with respect to that shape. The total intensity is proportional to

$$I(\omega) = \sum_{a,b} I_{ab}(\omega). \quad (7)$$

In the present approximation only the ground doublet Γ_6 is appreciably occupied at low T and the Fermi function is practically equal to one for the values of ω considered. In the next section we calculate Eq. (7) for $\text{MgO}:\text{Co}^{2+}$ at $T=0$ K.

By proper choice of ϵ' and ϵ , the irreducible representations E_g and T_{2g} of the Raman tensor \mathbf{R}_{ab} can be separated. In the E_g configuration (and $T \sim 0$ K) we only have transitions from the ground doublet Γ_6 to the two quadruplets Γ_8 and Γ_8' , and in the T_{2g} configuration the Γ_6 to Γ_7 transition should also appear. Experiments in the two configurations give information about the relative values of the different irreducible components of the Raman tensor: we shall see that the T_{2g} components appear to be rather smaller than the E_{2g} ones.

D. The line shape for $\text{MgO}:\text{Co}^{2+}$

In this section we calculate the line shape [Eq. (7)] employing a rather schematic phonon spectrum. We assume that the frequency $\omega(\mathbf{q}s)$ does not depend on the \mathbf{q} direction and that both sets of acoustical and optical modes are triply degenerate, with a frequency density given by a rather simple analytical expression. The polarizations are assumed to be strictly longitudinal or transversal; a reasonable approximation that substantially simplifies the angular averages. Replacing the sum over modes by an integration in \mathbf{q} space with the usual $V/8\pi^3$ density of modes the following relation holds:²⁹

$$\int \sum_s |T_{qs}^\gamma|^2 d\Omega_q = 4\pi [1 - \sin(2Rq)/2Rq], \quad (8)$$

where R is the lattice parameter of MgO . From the rather particular polarizations assumed above it follows that the sum over polarizations s can be restricted to the three

acoustical or to the three optical phonons. We introduce the frequency density of phonons $\rho_j(\omega)$, where the contribution of the acoustical phonons ($j=A$) has been separated from that of the optical ($j=O$) ones. With these approximations the self-energy [Eq. (5)] becomes

$$D_{aa'}(\omega) = C \sum_{\gamma,j,c} |V_\gamma|^2 [|\tau_{ca}^\gamma|^2 F_j(\omega_{a'c} - \omega) - |\tau_{a'c}^\gamma|^2 F_j(\omega - \omega_{ca})], \quad (9)$$

where $C=1/(2\hbar m_0)$ and the sum over j adds the separate contributions of the acoustic and optical phonons. The complex function F_j is

$$F_j(x) = f_j(x) + ig_j(x), \quad (10)$$

where

$$f_j(x) = \int \frac{[1 - \sin(2Rq)/2Rq] \rho_j(\omega_q)}{[\omega_q(\omega_q - x)] d\omega_q} \quad (11)$$

and

$$g_j(x) = \pi [1 - \sin(2Rq)/2Rq] \rho_j(\omega_q) / \omega_q |_{\omega_q=x}.$$

In these expressions it is necessary to give \mathbf{q} as a function of ω_j . We have then employed for each branch j a monotonic dispersion relation $\omega_j(q)$ that can be easily inverted and is compatible with the analytic frequency density of phonons discussed below.

Unless $\gamma=A_1$ the last two terms of Eq. (5) vanish when $a=\Gamma_6$ because then $\tau_{aa}^\gamma=0$. It then follows that these terms do not contribute to Eq. (9) at low T , because only Γ_6 is appreciably occupied and we have also shown in subsection C that the contribution of the vibrational mode A_1 to Eq. (9) can be neglected.

We have approximated the density of phonons calculated by Peckham³⁰ by the sum of two continuous curves $\rho_j(\omega)$ that give separate contributions for A and O phonons. Each $\rho_j(\omega)$ is different from zero in two intervals and in each of them it is described by the function

$$\rho(\omega) = N[a + b(\omega - \omega_0)^c], \quad (12)$$

which satisfy $\int \rho_j(\omega) d\omega = N$. In Table I we give the four sets of a , b , c , and ω_0 together with the intervals in which Eq. (12) assumes those values. We can now compute the two frequency densities, which are plotted in Fig. 2 together with the theoretical results of Peckham.³⁰ The approximate $\rho_j(\omega)$ we have employed were sufficient to reproduce the important features of the observed Raman spectrum, and it did not seem worthwhile to repeat the calculation with more accurate analytic expressions.

Several parameters are necessary to calculate $D_{aa'}(\omega)$. For the energy separation between the four levels Γ_6 , Γ_8 , Γ_8' , and Γ_7 in the absence of JT interaction we will employ $E_8 - E_6 = 330 \text{ cm}^{-1}$, $E_8' - E_6 = 890 \text{ cm}^{-1}$, and $E_7 - E_6 = 935 \text{ cm}^{-1}$. These values have been obtained from the spin-orbit interaction of the free ion ($\lambda = -180 \text{ cm}^{-1}$) together with values of the cubic crystal field and of atomic parameters estimated from optical measurements of Low.¹¹ We have also included in the calculation a rather small degree of covalency between Co^{2+} and the

TABLE I. Values of the constants employed in the analytic density of phonons $\rho_j(\omega) = N[a + b(\omega - \omega_0)^c]$.

j	a (10^{-1} s^{-1})	b (10^{-2} s^{-1})	c	ω_0 (10^{12} Hz)	Interval (cm^{-1})
A	0.0	0.2024	7.101	0.0	0–287
A	0.5607	0.6675	0.2682	54.0	287–567
O	0.0	3.107	1.0	64.1	340–413
O	0.6833	2.481	0.1652	77.9	413–703

six nearest O^{2-} , which changes the values of those energy levels. With the inclusion of the dynamical JT effect, the large degree of covalency required in early works¹¹ to fit the experimental g factor of the Γ_6 doublet was markedly reduced.^{31,32} We employ a value intermediate between those of Refs. 31 and 32 because it gives a better fit of our calculated spectra with the experimental ones.⁵ More details of the calculation of these energy levels, which are very similar to those employed by Ray and Regnard,³¹ are given by Peixoto and Foglio.¹⁹

The matrix elements τ_{ab}^γ that appear in the JT interaction have been given by Foglio¹⁴ and Tucker.³³ The values of V_E and V_T have been obtained from the effect of applied stress on the EPR lines of the Γ_6 lines. The values quoted are $V_E = 2.04 \times 10^{11} \text{ cm}^{-1}/\text{cm}$ and $V_T = 0.34 \times 10^{11} \text{ cm}^{-1}/\text{cm}$ with a 20% relative error. As V_T is rather smaller than V_E , its effect is not very important, so we allowed V_E to vary between the bounds of the quoted 20% error. In particular, if we compute the $I_{ab}(\omega)$ that corresponds to the two transitions from Γ_6 to Γ_8 and Γ_8 , the relative spectrum for the E_g configuration would be obtained by adding the two together weighted by the appropriate components of the corresponding Raman tensors. As we do not know these tensors, we assumed

that they are both equal and found that $V_E = 2.4 \times 10^{11} \text{ cm}^{-1}/\text{cm}$ reproduce the experimental peaks that are close to 300 cm^{-1} . This spectrum is plotted in Fig. 3 together with the experimental one.⁵ The two agree fairly well, although the relative intensity of the two calculated peaks (in the 300 cm^{-1}) is inverted with respect to the experimental ones. The correct relative intensities of these two peaks was obtained for $V_E = 2.8 \times 10^{11} \text{ cm}^{-1}/\text{cm}$ but the agreement with the position of the lines was somewhat impaired.³⁴

In Fig. 4 we show the curve for the transitions $\Gamma_6 \rightarrow \Gamma_7$ calculated with the same V_E employed in Fig. 3. This line should appear in the T_{2g} configuration together with the $\Gamma_6 \rightarrow \Gamma_8$ and $\Gamma_6 \rightarrow \Gamma_8'$ transitions, but no lines were observed experimentally.⁵

III. DISCUSSION

The Raman spectrum of $\text{MgO}:\text{Co}^{2+}$ has been assigned by other authors^{2–5} to one-phonon transitions that be-

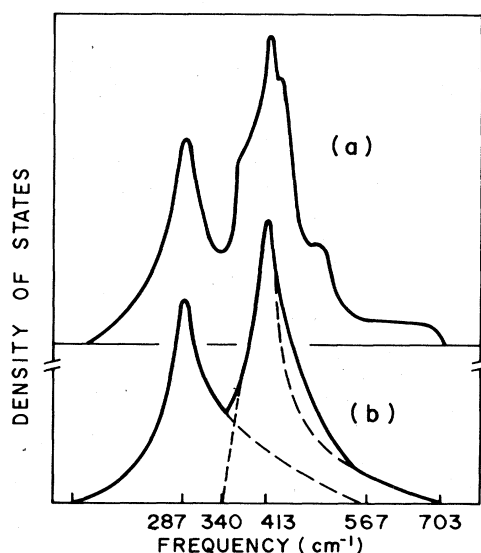


FIG. 2. One-phonon density of states in the MgO : (a) The curves computed by Peckham; (b) our approximation, where the dotted lines represent the acoustic and optical contribution.

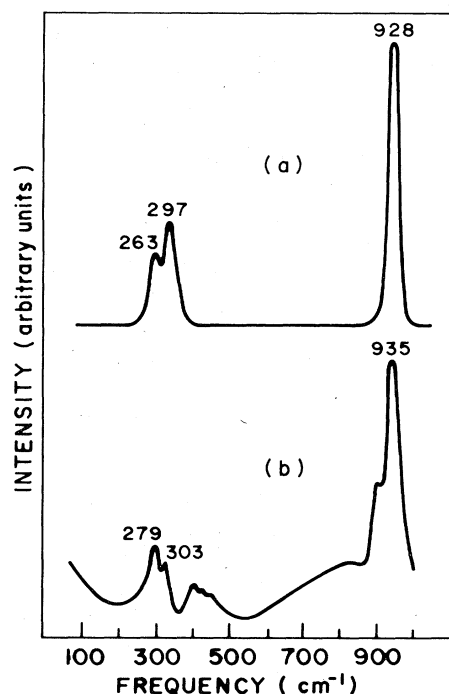


FIG. 3. Raman spectrum of the $\text{MgO}:\text{Co}^{2+}$ in the E_g configuration: (a) Electronic contribution as calculated in the present work; (b) experimental curve obtained by Guha at 18 K.

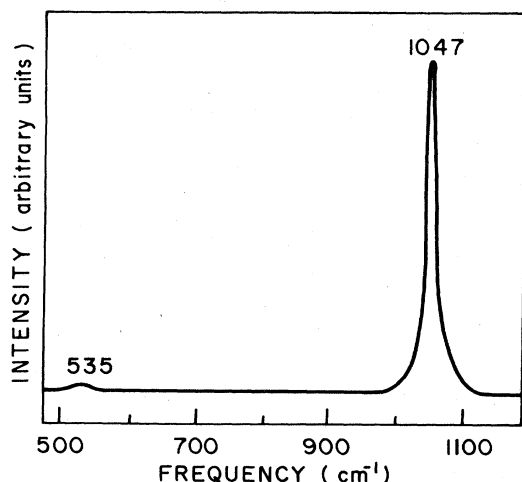


FIG. 4. Raman intensity for the electronic transitions $\Gamma_6 \rightarrow \Gamma_7$ calculated with our model.

come allowed because the impurities break the lattice translational invariance as well as the inversion symmetry of the remaining ions of the crystal. Mon² and Billat *et al.*^{3,4} do not give any arguments in favor of this interpretation, but Guha⁵ has studied the temperature dependence of the experimental peaks at 278.5 cm⁻¹, 304.75 cm⁻¹, and 935.7 cm⁻¹, concluding that the first two lines were of the one-phonon type. In his Fig. 2, the intensity of all these peaks decreases when T increases, and he states that the first two follow the $[1 - \exp(-\hbar\omega/k_B T)]$ law. This statement is rather puzzling, since the integrated intensity should be proportional to the number of phonons with frequency ω , which increases when T increases and which is given by the inverse of the law quoted by Guha. If the intensity plotted were that of the experimental peak height, their temperature dependence would not mean much because the corresponding dependence of the linewidth with temperature is not given by Guha. It is also not clear why he states that the temperature dependence he observes for the 935.7-cm⁻¹ line implies an electronic transition. Mon² and Billat *et al.*³ had already made that assignment because there are no phonons with that energy, and it could not be a localized mode because the mass of Co is much larger than that of Mg. It is then clear that one cannot reject the possibility of an electronic mechanism on the basis of the existing experimental evidence.

Wagner and Koidl³² have recently interpreted the inelastic scattering of neutrons by MgO:Co²⁺ employing the dynamical JT coupling of the Co²⁺ to a single E mode. From the agreement observed with the experimental results they conclude that the neutron resonances at 34.5 and 38.5 meV are electronic. As in their experiment, the coupling between the system and the probe is different from that in the Raman scattering, we should not consider this result as decisive, though it certainly corroborates our model.

The Raman scattering from Co²⁺-doped cubic KZnF₃ has been recently interpreted as of electronic origin by

Lockwood *et al.*⁹ In trigonal CoBr₂ both phononic and electronic bands have been assigned by Lockwood *et al.*⁸ and they have even observed lines with temperature-dependent intensities starting from an excited electronic state. In this problem the best model was a full 120-state $3d^7$ calculation of the energy levels, though an effective Hamiltonian in second order gave equally good agreement with the observed transition energies; but differed in their prediction of the ${}^4T_{1g}({}^4F)$ manifold g values, indicating that the $3d^7$ model is the best one.

Raman scattering from Fe²⁺ compounds has also been assigned to electronic processes: the cases of FeCl₂ and FeBr₂ are particularly interesting because the best (and accurate) description of all levels within the ${}^5T_{2g}({}^5D)$ manifold required the introduction of the dynamic JT effect. The full lattice model of Abou-Ghantou *et al.*^{16,17} based on the transformation method of Stevens³⁵ was employed in the treatment of this effect. The formalism looks exactly like that used when only the coupling between the magnetic ion and its nearest neighbors is considered; an effective Hamiltonian with the same form but with different expressions for the reduction factors is obtained. Johnstone *et al.*⁷ adjusted the parameters of their effective Hamiltonian, including the reduction factors, by minimization of the root-mean-square deviation of the experimental from the calculated values. A similar calculation was tried⁸ for CoBr₂, but contrary to what was found for Fe²⁺, the CoBr₂ data were not reproduced in a dynamical model.

The shape of the Raman line is not given in these full-lattice calculations while our GF formalism provides an approximate description of that shape. Stevens and Persico³⁶ and Van Eekelen and Stevens³⁷ also employed decoupling procedures of GF to study the EPR line shape of a triplet coupled to the lattice through the JT interaction, but no splitting was observed in their case. In our problem we have a more complex electronic structure of 12 states, and the process is of second order in the interaction with the radiation rather than being a first-order one. Nevertheless, the GF we have to calculate when we employ the approximate formula derived in Sec. II are basically of the same type employed by the authors mentioned above^{36,37} (we can express GF of the type $\langle\langle S_j; S_j \rangle\rangle$ as linear combination²⁴ of our $\langle\langle X_{aa}; X_{bb} \rangle\rangle_\omega$).

In our case, the rather asymmetric line shape obtained, is a consequence of the ω dependence of the self-energy; we would have obtained a superposition of Lorentzians if we had employed a constant self-energy for each transition.

There are several comments to be made when the experimental spectra are compared with our GF calculation.

(a) The simple superposition of the single-phonon spectrum calculated by Guha⁵ plus the two $\Gamma_6 \rightarrow \Gamma_8$ electronic transitions of the Co²⁺ in the MgO crystal without JT interaction would give a spectrum rather different from what is observed in the E_g configuration. As pointed out by Guha,⁵ an extra line (electronic) should be observed in the 300-cm⁻¹ region. In our model without JT the line should appear at 330 cm⁻¹ (329 cm⁻¹ for Guha), and the line observed at 935.7 cm⁻¹ should appear in our model at 890 cm⁻¹ (859 cm⁻¹ for Guha). If one would invoke co-

valency to decrease the effective spin-orbit interaction, so that the 330-cm^{-1} line would be shifted to 300 cm^{-1} , the 890-cm^{-1} line should decrease to 809 cm^{-1} , which is clearly not acceptable (with Guha's value it should appear at 781 cm^{-1}). It is worthwhile to point out that from the magnetic susceptibility measurements, Cosee³⁸ estimated that the Γ_8 level should be at 306 cm^{-1} above the ground Γ_6 level, a value that agrees fairly well with our calculation.

One should note the contrasting behavior of covalency and of the JT interaction on the energy separation of the levels. While covalency decreases the effective spin-orbit interaction, so that in lowest order the ratio $(E_8 - E_6)/(E_8 - E_6)$ remains constant, the effect of the JT interaction is to decrease $E_8 - E_6$ and simultaneously increase $E_8 - E_6$. It is then clear that our model gives a consistent description of the experimental situation and that a superposition of a single-phonon spectrum with an electronic one without JT would not be satisfactory.

(b) In Fig. 3 one sees that for the E_g configuration in the 300-cm^{-1} region, both the experimental and the theoretical spectra show two well-defined peaks. The calculated doublet originates in the $\Gamma_6 \rightarrow \Gamma_8$ electronic transition, and a single line should appear in the absence of JT interactions. To understand the extra line notice first that the unperturbed $\Gamma_6 - \Gamma_8$ energy separation is very close to a sharp maximum of the density of phonons. We could then imagine an oversimplified model consisting of a single phonon interacting with a pair of electronic levels that have an excitation energy close to that of the phonon. This interaction gives two vibronic states with energies that are fairly close; both of them have a large component of the excited electronic state times the zero-phonon vibrational state and would therefore give a large contribution to the electronic Raman scattering. If the interaction between the phonon and the electronic part were absent, only a single (electronic) line would appear, and the other (phononic) line would have zero intensity. This effect was not obtained in the calculation of Van Eekelen and Stevens³⁷ because for the values of ω that are of interest in EPR the phonon spectrum is rather smooth and it is the rather abrupt changes of the phonon density in the 300-cm^{-1} region that makes the doublet appear in our calculation.

(c) As noted in Sec. IID, the experimental and calculated doublet discussed above have their relative intensities inverted. In our calculation, only a part of the interaction of the system with the radiation was considered, and as discussed in Sec. IIB, we believe that the part we omitted is fairly well described by the theories that only consider one-phonon scattering.²⁻⁵ In Fig. 4 of Guha's paper, the contribution of the Co^{2+} nearest neighbors to this type of Raman scattering shows a rather sharp peak in the 280-cm^{-1} region. Subtracting this type of contribution from the experimental spectrum one could reproduce the relative intensities of the doublet calculated with GF. The nearest-neighbor calculation of Guha has also a broad structure in the 400-cm^{-1} region that is missing from our GF calculation.

(d) The theoretical GF spectrum shows much less structure than the experimental one. As discussed above, the

part omitted in our calculation, as well as the two-phonon spectrum that is present even in pure MgO, could be the reason for most of the missing structure. A plot of the spectrum of pure MgO against that of the Co^{2+} -doped crystal is shown by Mon² in his Fig. 1, indicating that the two-phonon spectrum might indeed contribute in the region above 700 cm^{-1} . The two-phonon contribution has a different temperature dependence than the single-phonon one, and it is less important at low temperatures.

The lack of structure of our GF calculation close to the experimental 935-cm^{-1} peak is not too surprising since due to our decoupling procedure the self-energy only includes processes in which a single phonon is created or destroyed (there are no phonons in the 935-cm^{-1} region).

(e) The experimental spectrum in the T_{2g} configuration is very weak, although the three electronic transitions starting from Γ_6 are allowed. The absence of a spectrum in this configuration was also reported by Lockwood *et al.*⁹ in Co^{2+} -doped KZnF_3 , and they concluded that the T_{2g} transitions have vanishing low Raman cross section compared with those of E_g configuration. It seems that this is also the case for $\text{MgO}:\text{Co}^{2+}$.

(f) In our estimation of the theoretical electronic levels unperturbed by the JT interaction, we only considered the 12 states of $^4T_{1g}(^4F)$, but Lockwood *et al.*⁸ needed the 120 states of $3d^7$ to fit the spectrum of CoBr_2 . This allows the use of energy values slightly different from those employed in Sec. IID, which could improve the agreement between our calculated spectrum and the experimental one, but we have not attempted this calculation.

IV. CONCLUSIONS

We have employed the JT interaction of Co^{2+} with lattice phonons to calculate the line shape of the electronic Raman spectrum of $\text{MgO}:\text{Co}^{2+}$. We have derived most of the model parameters from independent experimental measurements reported in the literature, and the Raman spectrum calculated with our model agrees fairly well with the experimental one.

When the BOA is valid, there is a clear distinction between the electronic and the single-phonon Raman scattering, but even with a weak JT interaction it becomes rather difficult to make this distinction when the phonons and the electronic excitations have fairly close energies. Nevertheless, we separated the interaction between the system and radiation in two parts so that each of them contribute through only one of the two types of mechanisms when the JT interaction is neglected. These two contributions are then complementary and in our model the main features of the spectrum are given by the calculated electronic scattering, while the phononic part contributes to most of the smaller details of the spectral structures particularly above 400 cm^{-1} . Although we have estimated that interference effects between the two probability amplitudes are small, they would not be excluded in principle. A more elaborated model in which the two contributions are calculated simultaneously should be employed to study this type of effect.

We are extending our calculation of the line shape to higher temperatures, to estimate the possible interest of

performing new measurements as a function of T . Another theoretical aspect we are considering is an estimation of the terms R_{ab} by employing the existing information about energy levels and stationary states of Co^{2+} . As discussed in (e) of Sec. III, the weakness of the spectrum in the T_{2g} configuration is not limited to the case of $\text{MgO}:\text{Co}^{2+}$ and it might be possible to find out why it occurs.

We are also considering the feasibility of a resonant Raman experiment that would make possible the observation of the electronic spectrum in the T_{2g} configuration. Resonance enhanced electronic Raman scattering of Fe^{2+} has been reported³⁹ for $\text{CdI}_2:\text{Fe}^{2+}$ and it might be possible to

perform a similar type of experiment in Co^{2+} -doped crystals.

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- ¹R. T. Harley, J. B. Page, and C. T. Walker, *Phys. Rev. B* **3**, 1365 (1971).
- ²J. P. Mon, *Phys. Lett.* **36A**, 479 (1971).
- ³A. Billat, R. Valet, and J. P. Mon, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flamarion, Paris, 1971), pp. 301–303.
- ⁴A. Billat, J. P. Mon, and M. Voisin, *Phys. Status Solidi B* **67**, 335 (1975); in *Proceedings of the Third International Conference on Light Scattering in Solids*, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flamarion, Paris, 1978), pp. 582–586.
- ⁵S. Guha, *Phys. Rev. B* **21**, 5808 (1980).
- ⁶M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
- ⁷I. W. Johnstone, D. J. Lockwood, and G. Mischler, *J. Phys. C* **11**, 2147 (1978).
- ⁸D. J. Lockwood, G. Mischler, I. W. Johnstone, and M. C. Smidt, *J. Phys. C* **12**, 1955 (1979).
- ⁹D. J. Lockwood, N. L. Rowell, and W. J. L. Buyers, in *Proceedings of the VII Conference on Raman Spectroscopy*, edited by W. F. Murphy (North-Holland, New York, 1980), pp. 154–155.
- ¹⁰D. J. Lockwood, in *Light Scattering in Solids III*, edited by M. Cardona and G. Güntherodt (Springer, New York, 1982), pp. 59–92.
- ¹¹W. Low, *Phys. Rev.* **109**, 256 (1958).
- ¹²H. A. Jahn and E. Teller, *Proc. R. Soc. London, Sect. A* **161**, 220 (1937); H. Jahn, *ibid.* **164**, 117 (1937).
- ¹³A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).
- ¹⁴M. E. Foglio, Ph.D. thesis, Bristol University, 1962.
- ¹⁵F. S. Ham, *Phys. Rev.* **138**, A1727 (1965).
- ¹⁶M. Abou-Ghantou, C. A. Bates, P. E. Chandler, and K. W. H. Stevens, *J. Phys. C* **7**, 309 (1974); M. Abou-Ghantou, C. A. Bates, and K. W. H. Stevens, *ibid.* **7**, 325 (1974).
- ¹⁷C. A. Bates, *Phys. Rep.* **35C**, 187 (1978).
- ¹⁸J. H. Van Vleck, *Physica (Utrecht)* **26**, 544 (1960).
- ¹⁹L. T. Peixoto and M. E. Foglio, *Rev. Bras. Fis.* **13**, 564 (1983); L. T. Peixoto, Ph.D. thesis, Universidade Estadual de Campinas, 1983.
- ²⁰F. S. Ham, W. N. Schwarz, and M. C. O. Brien, *Phys. Rev.* **185**, 548 (1969).
- ²¹J. Hubbard, *Proc. R. Soc. London, Ser. A* **285**, 542 (1965).
- ²²S. B. Haley and P. Erdos, *Phys. Rev. B* **5**, 1106 (1972).
- ²³M. E. Foglio, *Phys. Status Solidi B* **86**, 459 (1978); *ibid.* **87**, 87 (1978).
- ²⁴M. E. Foglio, *J. Phys. C* **11**, 4171 (1978).
- ²⁵M. E. Foglio, *J. Raman Spectrosc.* **10**, 52 (1981).
- ²⁶R. Loudon, *Adv. Phys.* **13**, 423 (1964).
- ²⁷R. M. Martin and L. M. Falicov, *Light Scattering in Solids*, edited by M. Cardona (Springer, Berlin, 1975), pp. 79–145.
- ²⁸D. N. Zubarev, *Usp. Fiz. Nauk.* **71**, 71 (1960) [*Sov. Phys.—Usp.* **3**, 320 (1960)].
- ²⁹N. G. Koloskova and P. I. Kochelaev, *Fiz. Tverd. Tela (Leningrad)* **9**, 2948 (1967) [*Sov. Phys.—Solid State* **9**, 2317 (1968)].
- ³⁰G. Peckham, *Proc. Phys. Soc. London* **90**, 657 (1967).
- ³¹T. Ray and J. R. Regnard, *Phys. Rev. B* **9**, 2110 (1967).
- ³²V. Wagner and P. Koidl, *J. Magn. Magn. Mater.* **15–18**, 33 (1980).
- ³³E. B. Tucker, *Phys. Rev.* **143**, 264 (1966).
- ³⁴Within the uncertainties of the assumptions employed to derive V_E and V_T , the error in these coefficients might easily be much larger than the 20% quoted in the text.
- ³⁵K. W. H. Stevens, *J. Phys. C* **2**, 1934 (1969).
- ³⁶K. W. H. Stevens and F. Persico, *Nuovo Cimento* **41A**, 37 (1966).
- ³⁷H. A. M. Van Eekelen and K. W. H. Stevens, *Proc. Phys. Soc. London* **90**, 199 (1967).
- ³⁸P. Cosee, *Mol. Phys.* **3**, 125 (1960).
- ³⁹I. W. Johnstone and L. Dubicki, in *Proceedings of the VII Conference on Raman Spectroscopy*, edited by W. M. Murphy (North-Holland, New York, 1980), pp. 152–153.